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Patent application in accordance with § 44 PatG has been filed

(54) Process for the production of a flexible and abrasion-resistant coating and clear lacquer  
for use in this process

(57) A hydrolyzable silane-based lacquer is  
described which after curing results in highly  
abrasion-resistant and flexible coatings and is  
obtainable in that one converts one or more  
hydrolyzable silicon compounds, which exhibit an  
epoxy ring, with water in a specific quantity range.  
The curing occurs preferably thermally after addition  
of a tertiary amine, in particular of an N-  
alkylimidiazole, as polymerization initiator for the  
epoxy groups. Particularly advantageous results are  
obtained when a cyclical carboxylic acid anhydride is  
used in addition to the tertiary amine.

## Description

The present invention relates to a process for the production of a flexible and abrasion-resistant coating and clear lacquer for use in this process as well as to the production of such a lacquer.

In comparison to purely organic coating systems, lacquer formulations containing silane, which were produced through conversion of hydrolyzable silicon compound with water or water-splitting media, exhibit distinctly better abrasion behavior and higher scratch proofness. They are, however, as a rule brittle and are inclined to stress cracks, for which reason only rigid molded solids can be scratch-proofed with them. Up to the present no lacquers are available for flexible substrates which combine in themselves the good abrasion properties of lacquer formulations containing silane and a high flexibility in the dried and/or cured state.

The task, therefore, of the present invention lay in making available a hydrolyzable silane-based lacquer which results in a coating with good abrasive behavior and high flexibility and, consequently, is suited for the coating not only of rigid bodies but also for coating mobile substrates, like films for example.

The task was solved in accordance with the invention through a process for the production of a hydrolyzable silane-based lacquer which is characterized in that one or more hydrolyzable compounds of the general formula(I)



in which the R residues, which can be identical or different, are selected from hydrolyzable (i.e., water-splittable) groups, hydroxy groups and non-hydrolyzable (i.e., nonwater-splittable) groups, in which at least some of the nonhydrolyzable groups present exhibit an epoxy ring and the molar ratio of hydrolyzable groups present to epoxy groups is 6 : 1 to 0.5 : 1; and/or corresponding oligomers formed through hydrolytic condensation are converted with water at a maximum temperature of 50°C, preferably 0 to 30°C and, in particular, room temperature, in which case a molar ratio of water to hydrolyzable groups present of 1 : 1 to 0.4 : 1 is selected.

The subject matter of the invention is also the lacquer which can be produced in accordance with the process and the use of same for the coating of substrates.

The hydrolyzable groups R in the above general formula(I) are preferably selected from halogen (F, Cl, Br and I, in particular Cl and Br), alkoxy (in particular C<sub>1-4</sub>-alkoxy, such as, for example, methoxy, ethoxy, n-propoxy, i-propoxy and butoxy), aryloxy (in particular C<sub>6-10</sub>-aryloxy, for example phenoxy), acyloxy (in particular C<sub>1-4</sub>-acyloxy, such as, for example, acetoxy and propionyloxy) and alkylcarbonyl (for example acetyl).

In addition to the above-mentioned, preferred hydrolyzable groups R, water and alkoxy residues with 5 to 20, in particular 5 to 10, carbon atoms and halogen- and alkoxy-substituted

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alkoxy groups (like, for example,  $\beta$ -methoxyethoxy) can also be mentioned as additional, likewise suitable groups.

Because the hydrolyzable groups R are practically no longer present in the end product but, rather, are lost through hydrolysis, in which case the hydrolysis product must also be removed sooner or later in a suitable manner, such hydrolyzable groups R are particularly preferred which carry no substituents and which lead to hydrolysis products with low molecular weight, like, for example, lower alcohols like methanol, ethanol, propanol, n-, i-, sec- and tert-butanol.

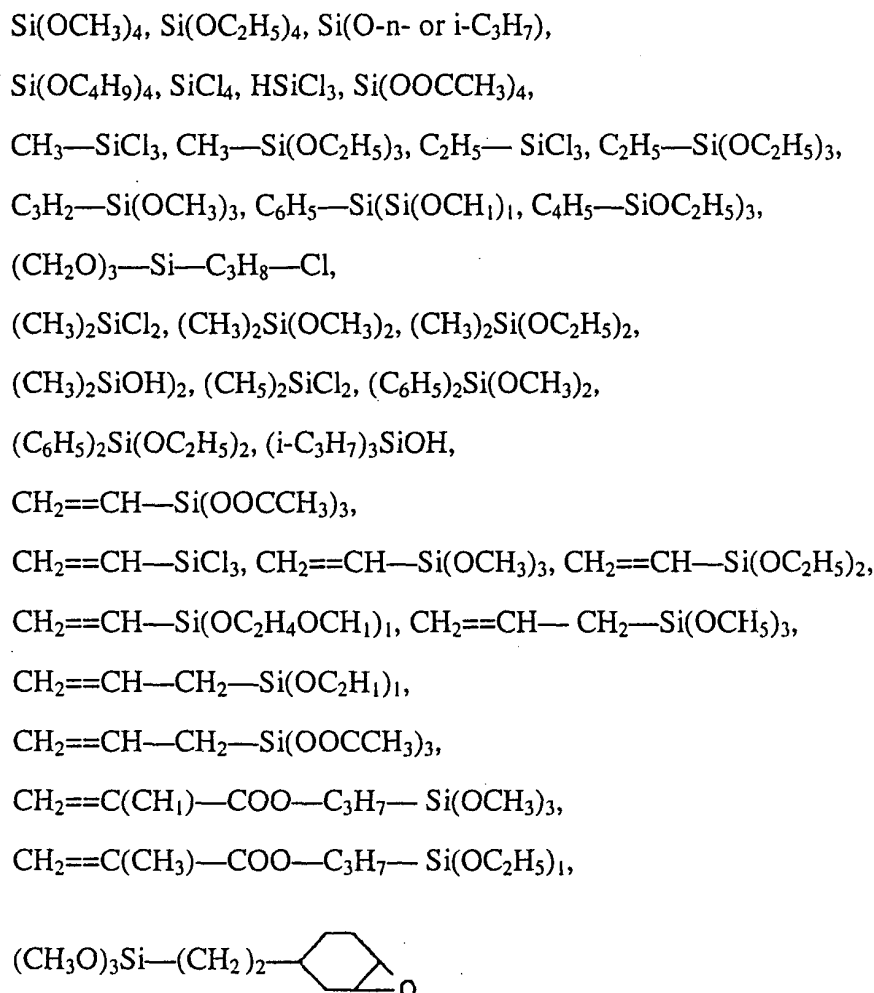
Because it is intended that the compounds of the general formula(I) in question be hydrolyzable compounds, it is obvious in and of itself that in these compounds, in each case, at least one of the groups R must be a hydrolyzable group. Preferably, however, compounds are used which exhibit at least two R hydrolyzable groups in which compounds with three or four hydrolyzable groups R are particularly preferred. Because, in accordance with the invention, nonhydrolyzable groups R, which exhibit an epoxy ring, must be present, there is always at least one compound of the general formula(I) among the hydrolyzable compounds used in accordance with the invention which exhibits three hydrolyzable groups R at the most.

The nonhydrolyzable groups R in the general formula(I) are preferably selected from alkyl (in particular  $C_{1-4}$ -alkyl, such as, for example, methyl, ethyl, propyl and butyl), alkenyl (in particular  $C_{2-4}$ -alkenyl, like, for example, vinyl, 1-propenyl, 2-propenyl and butenyl), alkenyl (in particular  $C_{2-4}$ -alkenyl, like, for example, acetylenyl and propargyl) and aryl (in particular  $C_{6-10}$ -aryl, like, for example, phenyl and naphthyl), in which case the groups just mentioned if necessary can exhibit one or more substituents which are inert under the reaction conditions, like, for example, halogen and alkoxy. The above alkyl residues also include the corresponding cyclical and aryl-substituted residues, like, for example, cyclohexyl and benzyl, while the alkenyl and alkynyl groups can likewise be cyclical and the aryl groups named should also include alkaryl groups (like tolyl and xylyl). Particularly preferred nonhydrolyzable groups R, among which in accordance with the invention at least one residue must be found which exhibits an epoxy ring, are alkyl groups. The epoxy ring is preferably present in the form of a glycidyl substituent on one of the above-mentioned nonhydrolyzable groups R. Particularly preferred are glycidyloxy - (preferably  $C_{1-4}$ )-alkyl residues R. On account of its ready accessibility, gamma glycidyloxypropyltrimethoxy silane is the most preferred compound with epoxy group of the general formula(I).

The compounds of the general formula(I) can be batched entirely or in part in the form of precondensates, i.e., compounds which have arisen through partial hydrolysis of the compounds of the general formula(I), either by themselves or in the mixture with other hydrolyzable compounds, in the manner in which they will be described further below in greater detail. Oligomers of this kind, preferably soluble in the reaction medium, can be straight-chain or cyclical, low-molecular partial condensates (polyorganosiloxanes) with degree of condensation of, for example, approximately 2 to 100, in particular approximately 2 to 6.

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Concrete examples of compounds (the majority of which are commercially obtainable) of the general formula(I) which are preferably used in accordance with the invention, in addition to the above-mentioned gamma glycidyloxypropyltrimethoxysilane, are compounds of the following formulas:



These silanes can be produced in accordance with methods known to the art; cf. W. Noll, "Chemie und Technologie der Silicone" ("Chemistry and Technology of Silicons"), Verlag Chemie GmbH, Weinheim/Bergstraße (1968).

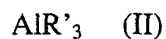
In the production process in accordance with the invention, the ratio of the hydrolyzable groups present in the compounds of the general formula(I) to the epoxy groups present lies preferably in the range from 4.5 to 1.5 : 1, in particular 3.5 : 1 to 2.5 : 1. In the simplest case, accordingly, only one single compound can be used which has three hydrolyzable groups R and one nonhydrolyzable group R with epoxy ring, e.g. gamma glycidyloxypropyltrimethoxysilane.

It is likewise preferred if, in the production process in accordance with the invention, the molar ratio of the water added to hydrolyzable groups in the compounds of the general

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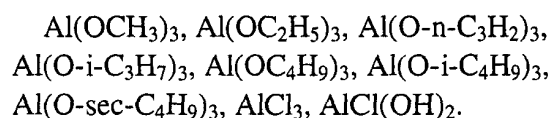
formula(I) lies in the range from 0.7 : 1 to 0.45 : 1. Particularly preferred is a ratio of 0.6 : to 0.5 : 1. The closer the ratio of water to hydrolyzable groups is to 0.5 : 1, the better the condensate waterproofness of the resulting (cured) coating.

Besides the silicon compounds of the general formula(I), hydrolyzable compounds with different central silicon atoms can also be used to a subordinate extent. If they used at all, these compounds, in the aggregate, preferably make up, however, less than 20 molar percent, in particular less than 10 molar percent of all base compounds batched. Preferred examples of different silicon central atoms are aluminum, titanium, zirconium, vanadium, tin, lead and boron. Such compounds with central atoms of this kind are especially possible which have groups R, as described above for the compounds of the general formula(I). However, attention must be given that, as a result of such different compounds of the compounds of the general formula(I), the desired properties, in particular abrasion resistance and flexibility, of the resulting coatings are not noticeably impaired. The aluminum compounds of the general formula(II)

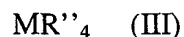


can be mentioned as those compounds possibly present (preferably in quantities up to 10 molar percent) in which the residues R', which can be identical or different, are selected from halogen, alkoxy, alcoxycarbonyl and hydroxy. With respect to the narrower (preferred) definition of these residues, reference can be made to the statements in connection with the hydrolyzable silicon compounds which are suitable in accordance with the invention. The groups just mentioned can also be entirely or partially substituted by chelate ligands (e.g., acetylacetone or acetoacetic ester).

Concrete examples of usable aluminum compounds are the following:



Suitable hydrolyzable titanium and zircon compounds which can be used in accordance with the invention (preferably in quantities up to 10 molar percent) are those of the general formula(III)



in which M stands for Ti or Zr and R'' is defined as R. Particularly preferred in the case of the compounds of the general formula(III) are those which have four hydrolyzable groups R''.

Concrete examples of zircon and titanium compounds which can be used are the following:

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$\text{TiCl}_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ,  $\text{Ti}(\text{O-i-C}_3\text{H}_7)_4$ ,  
 $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Ti}(\text{2-ethylhexoxy})_4$ ,  $\text{ZrCl}_4$ ,  $\text{Zr}(\text{OC}_2\text{H}_5)_4$ ,  
 $\text{Zr}(\text{OC}_3\text{H}_7)_4$ ,  $\text{Zr}(\text{O-i-C}_4\text{H}_7)_4$ ,  $\text{ZrOCl}_2$ ,  
 $\text{Zr}(\text{2-ethylhexoxy})_4$ .

As can be seen, in the case of the titanium and zircon compounds some of the residues bound to the central atom can be replaced by chelate ligands. The compounds already indicated above for Al, acrylic acid, methacrylic acid and the like can be mentioned as examples of chelate compounds of this kind.

It should also be mentioned in this connection that (hydrolyzable) titanium and zircon compounds, in particular the alcoholates, can also catalyze the epoxy ring opening and polymerization.

Additional hydrolyzable compounds which can be used in accordance with the invention to a subordinate extent (preferably under 5 molar percent) are, for example, boron trihalogenides and boron acetic esters (such as, for example,  $\text{BCl}_3$ ,  $\text{B}(\text{OCH}_3)_3$  and  $\text{BO}(\text{C}_2\text{H}_5)_3$ ), stannic tetrahalogenides and stannic tetraalkoxides (such as, for example,  $\text{SnCl}_4$  and  $\text{Sn}(\text{OCH}_3)_4$  and vanadyl compounds, such as, for example,  $\text{VOCl}_3$  and  $\text{VO}(\text{OCH}_3)_3$ .

As for the silicon compounds of the general formula(I), it also applies for the remaining hydrolyzable compounds which can be used in accordance with the invention that the hydrolyzable residues preferably lead to hydrolysis products which exhibit a low molecular weight. Preferred residues are, therefore,  $\text{C}_{1-4}$ -alkoxy (e.g., methoxy, ethoxy and propoxy) as well as halogen (in particular Cl).

In the presence of aluminum, titanium and/or zircon compounds in the mixture to be hydrolyzed, the above statements apply with respect to the ratios of the individual groups and compounds to each other respectively. It must furthermore be emphasized in this connection that the above-indicated ranges refer to monomers used, i.e., compounds not yet precondensed. As already mentioned above, precondensates of this kind can, however, be used in accordance with the invention, in which case these precondensates can be formed through the application of a single compound or through application of several compounds which can possibly also exhibit different central atoms.

The production of the lacquer in accordance with the invention can take place in a method which is standard in this field. If (during hydrolysis relatively chemically inert) silicon compounds are (practically) exclusively used, in most cases hydrolysis can occur in that one directly (preferably with stirring and in the presence of one of the catalysts defined in greater detail below) adds the quantity of water in accordance with the invention, at room temperature or with slight cooling, to the silicon compound or silicon compounds to be hydrolyzed which are present either as such or dissolved in a suitable solvent (see below) and subsequently stirs the resulting mixture for some time (e.g., one to several hours). In the presence of the more reactive compounds of aluminum, titanium and zircon, phased addition of the water is, as a rule, recommended. Independent of the reactivity of the compounds

present, hydrolysis takes place at a temperature not exceeding 50°C, preferably between 0°C and 30°C and/or the boiling point of the solvent possibly used. Preferably, no solvent is applied, in particular when the hydrolyzable groups R, R' and R'', which during hydrolysis lead to the formation of (lower) alcohols, like, for example, methanol, ethanol, propanol and butanol, are at issue. Otherwise (e.g., when using halogen silanes), suitable solvents are, for example, the above-mentioned alcohols, and ethers, preferably lower dialkylethers and diethylethers, THF, esters like acetic ester, and, in particular, butoxyethanol.

In accordance with a preferred specific embodiment of the present invention, the lacquer in accordance with the invention is produced in the presence of an acid or alkaline catalyst which, under the reaction conditions just described, produces practically no epoxy ring opening. Catalysts used preferably in accordance with the invention are proton-splitting compounds, e.g., halogen hydrogen acids (in particular HCl and H<sub>2</sub>CO<sub>3</sub> and/or CO<sub>2</sub>), organic carboxylic acids (e.g., formic acid and acetic acid) and inorganic bases and tertiary amines, like ammonia, alkali and alkaline-earth hydroxides (e.g., sodium, potassium or calcium hydroxide) and triethylamine. For reasons explained in greater detail below, if the lacquer is to be applied immediately, a tertiary amine, in particular one which is capable of initiating a polymerization at temperatures above 60°C of the epoxy groups, is preferred as a hydrolysis catalyst. Benzyldimethylamine and, in particular, N- (preferably C<sub>1-4</sub>)alkylimidazoles (e.g., N-methylimidazole and N-butylimidazol) can be mentioned as suitable examples for this.

In the presence of an acid hydrolysis catalyst, conversion of the compounds of the general formula(I) with water under the above-indicated conditions, in contrast to hydrolysis with an alkaline catalyst, always proceeds incompletely (as a rule, even under extremely acid conditions, only 50% of all hydrolyzable groups are actually hydrolyzed, such that this kind of lacquer can be stored at room temperature for months without noticeable viscosity increase. Under alkaline conditions, on the other hand, hydrolysis proceeds at least almost completely (in particular when substantially more than 0.5 moles of water are used per hydrolyzable group R) and the pH value influences only the time which is required for complete hydrolysis.

The lacquer produced as per above can then either be applied to a suitable substrate as such or following partial or almost complete elimination of the solvent used and/or of the solvent (e.g., of the alcohols resulting from hydrolysis of the alkoxides) formed during the reaction, or applied following the addition of a suitable solvent for viscosity-lowering purposes.

It can be necessary, in particular if the production of the lacquer occurred without solvent(s) and with the addition of water in the lower part of the range in accordance with the invention, to dilute the lacquer prior to application with a suitable organic solvent. Particularly suitable for this purpose are toluol, acetic ester, THF, glycol acid butyl ester, butoxyethanol, ethyleneglycomono- and diethylether and mixtures of the same. In this connection it should be borne in mind that the use of solvent generally decreases the condensate waterproofness (and, under some circumstances, abrasion resistance also) of the

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resulting coating. If the lacquer is nevertheless diluted with a solvent, then the quantity ratio of lacquer to solvent lies preferably in the range from 1 : 0.5 to 1 : 2.

If curing of the lacquer through radiation is intended, then a photoinitiator must be additionally added to the lacquer prior to application. An initiator is preferably also added if the curing is to occur thermally. Particularly preferred catalysts for thermal curing are described further below in greater detail.

Commercially available photopolymerization initiators, for example, can be used. Examples of these are the Irgacure type photoinitiators available from the Ciba-Geigy company and Merck company products marketed under the commercial name of Darocur. Particularly preferred UV initiators are those which are able to initiate a cationic polymerization of the epoxy groups. Among others, organic peroxides in the form of diacylperoxides, peroxide carbonates, alkylperesters, diacylperoxides, perketals, ketonperoxides and alkylhydroperoxides are possible. Concrete examples of such thermal initiators are dibenzoylperoxide, tert-butylperbenzoate and azobisisobutyronitrile.

The above initiators are added in usual quantities to the lacquer. Thus, for example, an initiator in a quantity from, e.g., 0.5 to 2 percent by weight (referenced to the total quantity) can be added to a lacquer with a solids content of 30 to 50 percent by weight.

The lacquer, if applicable (and preferably provided with an initiator), is then applied to a suitable substrate. Standard coating processes can be used for this coating, e.g., dipping, flow coating, pulling, casting, centrifuging, spraying or brush-application. Particularly preferred in accordance with the invention are dipping and pulling.

Before curing, the lacquer applied is preferably dried (at room temperature or slightly elevated temperature). Preferred coat thicknesses (in the cured state) lie between 5 to 20, in particular 10 to 15  $\mu\text{m}$ . Self-evidently, the process in accordance with the invention is not restricted to applying a single lacquer coat only to the substrate; rather, the possibility also exists of applying additional coats after the application and, if applicable, curing of a coat and thereby achieving multilayer structures.

After drying, if applicable, has been carried out, the lacquer applied to the substrate can, independent of the manner and/or presence of an initiator, be cured thermally or through radiation (e.g., with a UV radiator, a laser, etc.) in a manner known to the art.

In the case of thermal curing, curing temperatures are preferably at least 70°C, in particular at least 90°C. Particularly preferred ranges are 95 to 150°C and/or 110 to 140°C. In individual cases, the curing temperature depends, in particular, on the thermal stability of the substrate to be coated. Likewise, the required curing time can vary within a broad limit in function of the concrete curing conditions, e.g., from under a minute to several hours.

Plastic materials and metals are particularly preferred in accordance with the invention as the substrates to be coated, even though other substrates, e.g., made of glass or paper, can be coated in a satisfactory manner with the lacquer in accordance with the invention.



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Concrete examples for the above plastic materials are polyolefins (e.g., polyethylene, polypropylene, polystyrol), saturated, unsaturated, aromatic and aliphatic polyesters (like, for example, polymethylmethacrylate and polyethyleneterephthalate), polyethers, polycarbonates, polyamides, polyurethanes, rubber-like polymers, etc. Preferred plastic materials are polycarbonates, poly(meth)acrylates, rubber-like (coating)polymers (like, e.g., ABS polymers) and polyethyleneterephthalate.

Preferred metal substrates are those made of aluminum or copper. Owing to the high flexibility of the coatings produced from the lacquer in accordance with the invention, the coating of substrates which exist in flexible form, e.g., as films or foils, particularly offers many advantages.

In order to assure an excellent adherence of the coating on the substrate, it is recommended, as a rule, that the substrate be subjected, prior to coating, to a surface treatment, e.g., through leaching, priming with a primer, corona treatment, etc. It was surprisingly determined that, in the case of plastic substrates, such surface treatment can also be omitted and very good adhesion between substrate and coating nevertheless achieved.

In accordance with a particularly preferred specific embodiment of the present invention, in the above-described production of the lacquer in accordance with the invention, prior to, during or after conversion of the hydrolyzable (silicon) compound(s) with water at least one compound is added which does not, at least noticeably, impair (i.e., negatively influence) hydrolysis but which, on the contrary, possibly even catalyzes it and at temperatures above 60°C can initiate a (anionic) polymerization of the epoxy groups present. Tertiary amines, in particular dimethylbenzylamine and N-alkylimidazoles, have shown themselves to be particularly suitable for this purpose. As already mentioned above, these compounds can also catalyze the hydrolysis of the silicon compounds of the formula(I) such that, with the addition of these compounds before or during the conversion with water, a separate addition of another hydrolysis catalyst can be dispensed with. If a tertiary amine of the above kind is also used as a ring-opening and polymerization initiator, then the molar ratio of the epoxy groups present (used) to tertiary amine in the lacquer in accordance with the invention lies preferably in the range from 1 : 0.01 to 1 : 0.03. A particularly preferred range is 1 : 0.05 to 1 : .02, in which case the best results are achieved with a ratio of 1 : 0.1 to 1 : 0.15.

The use of tertiary amines, in particular N-alkylimidazoles, as polymerization initiators for the epoxy groups results in a cured coating with particularly satisfactory properties with respect to abrasion resistance and flexibility but also in terms of appearance, adherence to the substrate and condensate waterproofness. A further improvement of these characteristics can be achieved by using, in addition to the tertiary amine, at least another cyclical carboxylic acid anhydride which does not noticeably impair hydrolysis under the reaction conditions and is able to effect an epoxy ring opening at temperatures above 60°C, in which case the molar ratio of epoxy groups present (used) to acid anhydride is standardized, preferably in the range from 10 : 1 to 1 : 1, in particular 8 : 1 to 3 : 1.

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Hexahydrophthalic acid anhydride, phthalic acid anhydride, pyromellitic acid anhydride, methylnadic anhydride, HET acid anhydride, methyl-5-norbornen-2,3-dicarboxylic acid and succinic acid can be mentioned as concrete examples for suitable cyclical carboxylic acid anhydrides. If applicable, these acid anhydrides can also carry substituents like, for example, in the case of dodecyl-succinic acid anhydride. Particularly outstanding results are achieved with acid anhydrides which carry substituents containing silicon, in particular substituents of the general formula  $R_3Si$ -alkyl, like, for example, (3-triethoxysilylpropyl) succinic acid anhydride.

The use of a cyclical acid anhydride in combination with a tertiary amine results, for example, in a colorless coating which is further improved with respect to scratch resistance, UV stability, condensate waterproofness and adhesion to the substrate.

With the present invention a comparably simple process for the production of flexible and at the same time abrasion-resistant coatings on molded solids is made available in particular. It is particularly surprising that hydrolysis can occur in the simplest form. The coatings produced in accordance with the invention are of outstanding appearance, adhesion- and abrasive-resistant, condensate-resistant and show no stress cracking. They are far and away superior in their flexibility to conventional, polysiloxane-based coatings. Thin films, for example, can be provided with a coating the quality of which has hitherto been reserved for rigid substrates only.

The following examples are intended to further explain the present invention without, however, limiting its scope.

### Example 1

236 g (1 mole) gamma glycidyloxypropyltrimethoxysilane were stirred with 27.0 g (1.5 mole) water (pH 5.5) and 8.21 g (0.1 mole) N-methylimidazole for 3 at room temperature. Thereafter, the lacquer was applied through pulling to a polyethyleneterephthalate film, dried 10 minutes at room temperature and cured 90 minutes at 130°C. The structure-free, colorless, clear and condensation waterproof layer was highly flexible and after 100 cycles on the Taber abraser, exhibited a stray light loss of 1%. The flexibility radius of the 13  $\mu$ m-thin layer was 1 mm.

### Example 2

A polycarbonate plate was coated through dipping with the lacquer produced in accordance with Example 1, dried 10 minutes at room temperature and cured 90 minutes at 130°C. After 100 cycles on the Taber abraser, the resulting condensation waterproof layer exhibited a stray light loss of 1%. The cross-cut before and after the scotchtape test attained the value 0.

### Example 3

236 g (1 mole) gamma glycidyloxypropyltrimethoxysilane were stirred with 27.0 g (1.5 mole) water (pH 5.5) and 410 g (0.05 mole) N-methylimidazole for 3 at room

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temperature. After the addition of 152 g (0.05 mole) (3-triethoxysilylpropyl) succinic acid and a stirring time of 45 minutes at room temperature, the lacquer was diluted with butoxyethanol in a ratio of 1 : 0.5. The lacquer was applied through pulling to a polyethyleneterephthalate film, dried 10 minutes at room temperature and cured 45 minutes at 130°C. The structure-free, colorless, clear coating was of excellent appearance and after 100 cycles on the Taber abraser, exhibited a stray light loss of 1%. The flexibility radius of the 10 µm-thin layer was 1 mm.

### Example 4

A polycarbonate plate was coated through dipping with the lacquer produced in accordance with Example 3, dried 10 minutes at room temperature and cured 45 minutes at 130°C. A structure-free, colorless and clear coating of outstanding appearance resulted. The coating was condensate-resistant and after 100 cycles on the Taber abraser exhibited a stray light loss of 1%. The cross-cut before and after the scotchtape test attained the value 0.

### Example 5

Spectacle glass made of CR39 was scratch-proofed with the lacquer composition from Example 3 with the aid of the coating technology and curing conditions of Example 4. The structure-free, colorless, clear coating was of excellent appearance and condensate waterproofness. Stray light loss after 100 cycles on the Taber abraser was very low (1%). Adhesion between coating and substrate was also very good.

### Example 6

An aluminum sheet was coated through dipping with the lacquer composition from Example 3. The lacquer was thereafter dried 10 minutes at room temperature and cured 45 minutes at 150°C. The resulting coating was shown to be stable and condensate water resistant. It did not spall during deformation of the sheet metal.

### Example 7

Lead glass was coated through dipping with the lacquer composition from Example 3 and under the curing conditions described in Example 6. Following curing, a well-adhering, condensate waterproof coating of very good appearance was obtained.

### Example 8

47.3 g (0.2 mole) gamma glycidyloxypropyltrimethoxysilane were stirred with 3.29 g (0.2 mole) poly-propylmethoxysilane, 3.28 g (0.4 mole) N-methylimidazole and 10.8 g (0.6 mole) water (pH 5.5) for 16 hours. The resulting lacquer was diluted with butoxyethanol in a 1 : 0.5 ratio and applied through dipping to a polymethylmethacrylate plate. The lacquer was cured 90 minutes at 85°C and thereafter 10 minutes at 130°C. The structure-free, colorless, clear coating was condensate waterproof and after 100 cycles on the Taber abraser exhibited a stray light loss of 2.2%. The cross-cut before and after the scotchtape test was 0.

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### Example 9

47.3 g (0.2 mole) gamma glycidyloxypropyltrimethoxysilane were stirred with 5.40 g (0.3 mole) water (pH 5.5) for 16 hours. The storage-stable prehydrolysate obtained was mixed with 0.82 g (0.01 mole) N-methylimidazole. After 2 hours' stirring, 10.7 g methyl-5-norbornen-2,3-dicarboxylic acid (isomer mixture) was added and subsequently stirred for 30 minutes. Plates made of polystyrol were coated through dipping with the resulting lacquer, which was cured thereafter at 70°C. A well-adhering, colorless coating was obtained which was abrasion resistant (stray light loss 1%) and condensate water resistant.

### Example 10

236 g (1 mole) gamma glycidyloxypropyltrimethoxysilane were stirred with 27.0 g (1.5 mole) water (pH 5.5) for 16 hours at room temperature. The storage-stable partial hydrolysate thereby obtained was mixed, with ice cooling and intensive stirring, with a mixture of 32.8 g zirconium tetrapropylate and 8.61 g (0.1 mole) methacrylic acid. After 30 minutes one added 5.4 g (0.3 mole) drops of water and stirred another 60 minutes at room temperature. Thereafter, 1% 1-hydroxy-cyclohexylphenylketone, referenced to the total quantity, was added.

This lacquer was applied to a poly(diethyleneglycol-bis-allylcarbonate) plate previously treated with sufficiently high alternating stress (corona), precured 20 seconds with a UV radiator (2000 W) and final-cured 30 minutes at 130°C in the recirculating air drying chamber. A condensate water resistant (15 days condensate waterproofness test at 40°C), abrasion-resistant (stray light loss after 100 Taber abraser cycles 0.5%) and very good adhering coating (cross-cut before and after scotchtape test 0) resulted.

### Example 11

1 mole each of gamma glycidyloxypropyltrimethoxysilane was added with 1.5, 2.0, 2.50 and/or 3.0 mol water (pH 5.5) and stirred for 16 hours. After the addition of 0.1 mole N-methylimidazole and further 3 hours' stirring, the viscous, clear and colorless lacquers were ready to use and could be applied through dipping or pulling to substrates.

Polycarbonate disks (10 x 10 x 0.15 cm) were degreased with aqueous soap lye, dried 10 minutes at 130°C, blown dustfree with compressed air and through dipping respectively coated once with the lacquers obtained as above. In a second series of tests the substrates, pretreated in the same manner, underwent a surface activation through the application of a sufficiently high alternating stress (corona process).

The substrates coated with a thin, colorless and clear layer exhibited small surface structures which disappeared gradually after 10 minutes' predrying at room temperature. Curing took place for 3 hours at 130°C in a recirculating air drying chamber. Comparisons between corona-treated and untreated samples showed a slightly improved adhesion and condensate waterproofness if the surface had been activated before coating. For all cured

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lacquers, stray light loss after 100 cycles on the Taber abraser was 1% and the cross-cut between 0 and 1. Layer thicknesses were, on the average, 10  $\mu\text{m}$ .

If the lacquer was first applied one day after its production and cured, decreased condensate water resistance of the resulting coating was observed.

### Example 12

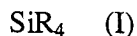
Dustfree-blown polyethyleneterephthalate films were coated through film dipping (15  $\mu\text{m}$ ) with the lacquers described in Example 11 which were predried 10 minutes and thereafter cured 3 hours at 130°C. The structure-free, colorless and clear coatings were highly flexible and after 100 cycles on the Taber abraser exhibited a stray light loss of only 0.8%. Adhesion of all lacquers was very good (cross-cut 0). Layer thickness decreased with increasing water content from 17  $\mu\text{m}$  to 13  $\mu\text{m}$ . Increasing lacquer water content resulted after 15 days' condensate waterproofness testing in the formation of fine hairline cracks. Consequently, the practically water-free lacquer (1.5 mole  $\text{H}_2\text{O}$ ) was best suited for the polyethyleneterephthalate film coating.

### Example 13

An aluminum film was coated with a water-free lacquer containing toluol which was produced using 1 mole gamma glycidyloxypropyltrimethoxysilane, 1.5 mole water and 0.1 mole N-methylimidazole. After curing, the coating exhibited excellent adhesion and very high mechanical stressability and did not spall even when the film was crumpled.

## Patent Claims

1. Process for the production of a hydrolyzable silane-based lacquer, **characterized in that** one or more hydrolyzable compounds of the general formula(I)



in which the R residues, which can be identical or different, are selected from hydrolyzable groups, hydroxy groups and non-hydrolyzable groups, in which at least some of the nonhydrolyzable groups present exhibit an epoxy ring and the molar ratio of hydrolyzable groups present to epoxy groups is 6 : 1 to 0.5 : 1; and/or corresponding oligomers formed through hydrolytic condensation are converted with water at a maximum temperature of, preferably 0 to 30°C and, in particular, room temperature, in which case a molar ratio of water to hydrolyzable groups present of 1 : 1 to 0.4 : 1 is selected.

2. Process in accordance with Claim 1, characterized in that the hydrolyzable groups are selected from halogen, alkoxy, aryloxy, acyloxy and alkylcarbonyl, in particular.
3. Process in accordance with any one of Claims 1 and 2, characterized in that the nonhydrolyzable groups are selected from alkyl, alkenyl, alkynyl and aryl residues, in

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which case some of these additionally exhibit an epoxy ring, preferably in the form of a glycidyl(oxy) substituent.

4. Process in accordance with any one of Claims 1 through 3, characterized in that the combinations of the general formula(I) comprise a glycidyoxyalkyltrialkoxysilane, preferably gamma glycidyoxypropyltrimethoxysilane.
5. Process in accordance with any one of Claims 1 through 4, characterized in that the ratio of hydrolyzable groups to epoxy groups is 4.5 : 1 to 1.5 : 1, in particular 3.5 : 1 to 2.5 : 1.
6. Process in accordance with any one of Claims 1 through 5, characterized in that the molar ratio of water to hydrolyzable groups 0.7 : 1 to 0.45 : 1, in particular 0.6 : 1 to 0.5 : 1.
7. Process in accordance with any of Claims 1 through 6, characterized in that the conversion is carried out with water in the presence of an acid or alkaline catalyst which, under the reaction conditions, practically effects no epoxy ring opening.
8. Process in accordance with Claim 7, characterized in that the catalyst is selected from halogen hydrogen acids, in particular HCl, organic carboxylic acids, in particular formic acid and acetic acid, inorganic bases and tertiary amines, in particular N-alkylimidazoles.
9. Process in accordance with any one of Claims 1 through 8, characterized in that prior to, during or after conversion with water at least one compound is added which does not, at least noticeably, impair hydrolysis but which at temperatures above 60°C or under the effect of radiation can initiate a polymerization of the epoxy groups present.
10. Process in accordance with Claim 9, characterized in that the compound is selected from tertiary amines, preferably benzyldimethylamine and N-alkylimidazoles, in particular N-methylimidazole.
11. Process in accordance with Claim 8, characterized in that the tertiary amine is added in such quantities that the molar ratio of epoxy groups batched to tertiary amine is 1 : 0.01 to 1 : 0.03, preferably 1 : 0.005 to 1 : .02, and in particular 1 : 0.1 to 1 : 0.15.
12. Process in accordance with any one of Claims 10 and 11, characterized in that prior to, during or after conversion with water one additionally adds at least one carboxylic acid anhydride which, under the reaction conditions, does not noticeably impair the hydrolysis and is able to effect an epoxy ring opening at temperatures above 60°C, in which case the molar ratio of epoxy groups present to acid anhydride is standardized preferably in the range from 10 : 1 to 1 : 1, in particular 8 : 1 to 3 : 1.
13. Lacquer, obtainable according to the process in accordance with any one of Claims 1 through 12.
14. Process to coat substrates with a flexible and abrasion-resistant coating, characterized in that one applies a lacquer in accordance with Claim 13 to the substrate

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and thereafter, possibly after the addition of a suitable catalyst, carries out thermal or radiation curing.

**15.** Process in accordance with Claim 14, characterized in that the lacquer, prior to application, is standardized to a suitable viscosity with an organic solvent, preferably selected from toluol, acetic ester, tetrahydrofurane, glycol acid butyl ester, butoxyethanol, ethylene glycomono- and diethylether and mixtures of the same.

**16.** Process in accordance with any one of Claims 14 and 15, characterized in that, prior to curing, the lacquer is dried, preferably at room temperature.

**17.** Process in accordance with any one of Claims 14 through 16, characterized in that the curing occurs thermally at temperatures of at least 70°C, preferably at temperatures from 95 to 150°C and, in particular, 110 to 140°C,.

**18.** Process in accordance with any one of Claims 14 through 17, characterized in that the substrate is selected from plastic materials, in particular polycarbonates, poly(meth)acrylates, rubber-like polymers and polyethyleneterephthalate, and metals, in particular aluminum and copper.

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